## ULMITE, A CONSTITUENT OF BLACK SANDSTONE.

## By Thos. Steel.

At various points along the coast of New South Wales there occur frequent outcrops of a black friable sandstone. The positions of some of these in the Richmond River district are indicated on maps published by the New South Wales Department of Mines (Ann. Rept., 1895, p. 151; 1896, p. 155).

At Tweed Heads a thick bed is exposed on the north bank of the river near the township, from which the sample described in this paper was obtained. There is no igneous rock near the deposit which is covered by a layer of ordinary sand of varying thickness. Water collected in wells dug in the overlying sand is brown in colour.

The rock is very friable, rubbing readily between the fingers to a sharp sand. On ignition a fragment crumbles to loose sand and becomes white. A portion heated in a glass tube yields water having a strongly acid reaction.

Under the microscope the rock is seen to be built up of worn sandgrains of fairly uniform size, each of which is covered with a thin dark-coloured film resembling a coat of varnish. Gentle friction suffices to remove the coating from the sand grains. On lixiviating the pulverised rock the dark coating can be readily separated and obtained quite free from sand and, when dry, forms a dark brown powder. Microscopically this shows as irregular flakes of varying thickness, the thinner ones being structureless and of a translucent brown colour, while the thick ones are black and opaque. The translatent flakes do not affect polarised light, and, as will be shown, chemical examination proves the substance to consist of humas or humic acid. The powder is readily and comptetely soluble in caustic potash, soda or ammonia, forming a clear deep-brown liquid which, on acidifying with subplurie or hydrochlorie acid, deposits a copious brown floceulent precipitate, leaving the solution moderately coloured. In strong sulphuric acid the dark powder dissolves readily, particularly on slightly warming, forming a clear, very dark brown solution, which, on being poured into a large volume of water, throws down a copious soft brown precipitate, leaving the solution only slightly coloured. In strong nitrie acid, the powder dissolves readily, but no precipitate is produced on dilution with water nor on neutralisation with alkalies. Even on boiling, the substance is only sparingly soluble in strong hydrochloric acid.

When the precipitate obtained by dilution of the solution in strong sulphuric acid is drained on a filter, the resulting slimy mass is readily soluble in water

and also in strong spirit, giving a solution resembling caramel. The water solution obtained in this way, when treated with barium hydrate or carbonate becomes colourless the substance being carried down along with the barium sulphate. The dark brown solution obtained by treating a dilute solution of soda or potash with excess of the substance, is readily precipitated with alcohol, the supernatant liquid having still, however. a fairly dark colour. A solution in potash, on neutralisation with subpluric acid, avoiding excess, remains clear and is precipitated by addition of alcohol. The precipitate may be thoroughly washed with dilute alcohol (Sp. Gr. 0.86), after which it dissolves readily in water, the solution so formed not being precipitated by alcohol, but, if a small amount of potash or soda be added, alcohol produces a copious precipitate, leaving the solution only slightly coloured. The aqueous solution of the alcohol-washed precipitate gives brown precipitates with most metallie salts, precipitation being complete, also with the hydrates and salts of barinm, calcium and strontium, with the alums, and with bromine water. Iodine, tannin and starch solutions produce no precipitate.

Amongst the few metallic salts which do not cause a precipitate are mercurie chloride and ammoniacal uitrate of silver. The colour is removed by shaking with hydrates of iron and alumina and with litharge, manganese dioxide, animal charcoal and ordinary soil, previous making no difference. When ignition oť the soil shaken with sand the solution is decolourised, the colour, however, being absorbed entirely by the fine elayey portion of the sand, the coarser grains being inert. The same applies to treatment with the black sandstone, after ignition, but if sand or soil is boiled with hydrochloric acid and washed so as to remove soluble mineral matters, the residue is quite inert.

The substance can be salted out of solution with a number of salts, sodium chloride and sulphate, ammonium sulphate, nitrate and chloride and others. leaving the solution but faintly coloured. From concentrated solutions, acetic acid causes practically complete precipitation in a well curdled form, but from dilute solutions the precipitate is slimy but equally complete.

The barium compound prepared by precipitating the water soluble preparation with baryta water, washing with alcohol, and drying, corrected for associated mineral matter, contains 41.3 per cent. barium oxide.

The pulverised air-dry rock yielded the following figures to proximate analysis :--

| Water                        | <br>1.63 |
|------------------------------|----------|
| Loss on ignition             |          |
| Sand                         |          |
| Soluble in hydrochlorie acid |          |
| Soluble in hydrochlorie acid | <br>.00  |

100.00

When the coating from the black sandstone is fixiviated until quite free from sand and air-dried, it has the following proximate composition:—

| ding dine direction | • IL 110.7 | full router and | - prominent |       |
|---------------------|------------|-----------------|-------------|-------|
| Water at 150°       | C          |                 |             | 17.3  |
| Loss on ignition    |            |                 |             |       |
| Mineral             |            |                 |             | 15.1  |
|                     |            |                 |             |       |
|                     |            |                 |             | 100.0 |

On boiling 0.5 gram with 50 c.e. N/10 caustic soda and titrating back with corresponding subpluric acid, 24.7 c.e. of neutralisation was obtained.

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This preparation, after drying at  $150^{\circ}$  C., calculated free from mineral matter, gave the results below, on ultimate analysis. Humus is known to have a somewhat variable composition according to source and method of preparation. When made from sugar, for instance, it may be quite free from nitrogen. For comparison 1 have inserted analyses of humus from a number of sources, references to which are given.

## Analyses of Humus Derived from Various Sources.

|          | 1.     | - 2,   | 3.     | 4.     |
|----------|--------|--------|--------|--------|
| Carbon   | 50.53  | 57.75  | 53.42  | 52.71  |
| Hydrogen | 5.67   | 5.43   | 5.16   | 3.98   |
| Oxygen   | 43.20  | 36.02  | 40.92  | 41.49  |
| Nitrogen | .60    | .80    | .50    | 1.82   |
|          |        |        |        |        |
|          | 100.00 | 100.00 | 100.00 | 100.00 |

1. Black sandstone. New South Wales.

2. Brown Peat. Watt's Dict. Chem., vol. viii., 1879, p. 649.

3. Decayed Fir wood. 4. Decayed Oak wood. 5. Jour. Chem. Soc., 1906, Abs. ii., p. 388.

A preparation of humus made by treating black soil from Blackheath, N.S. Wales, with potash, and precipitation with sulphuric acid, behaved in all respects in a manner identical with the black sandstone preparation.

I would propose the name Ulmite for this form of humus as found coating sandstone grains.

Samples of black sandstone were supplied to me by Mr. W. S. Dun, of the Department of Mines, from McAuley's lead, Esk River; Huka, Clarence River; and Sans Souci, near Sydney. They were in all respects similar to my specimen from Tweed Heads.

A similar coating to the above occurs on the rounded grains and pebbles of rock phosphate which constitute the surface "soil," four to six inches in depth, on Ocean Island (Jour. Soc. Chem. Ind., xl., 1921, p. 59r).